

Attorney Dkt: UCF-237

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: CHAI ET AL.

Serial No.: 09/506,160

Group No.: 2878

Utility Application Filed: 02/17/00

Provisional Application SN 60/120,500 Filed 02/18/99

Examiner: Constantine Hannaher

For: LUTETIUM YTTRIUM ORTHOSILICATE
SINGLE CRYSTAL SCINTILLATOR DETECTOR

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner of Patents
and Trademarks
Washington DC 20231

Sir:

BRUCE H.T. CHAI declares that:

1. I am a co-inventor of and familiar with the present U.S. Patent Application Serial No. 09/506,160 filed 02/17/00, which claims the benefit of priority to U.S. Provisional Application 60/120,500 filed 02/18/99 in the name of the University of Central Florida and Crystal Photonics, Inc., which is entitled: Lutetium Yttrium Orthosilicate Single Crystal Scintillator Detector, and I am familiar with the Official Action dated March 8, 2002 issued therein and with the prior art references cited in the Official Action, including U.S. Patent 4,958,080 to Melcher and Great Britain Patent Specification 1,336,518 to Watanabe et al.

2. I received a Bachelor of Science degree in Geology from National Taiwan University, Taipei, Taiwan, Republic of China in 1969. I received a Master of Philosophy degree in Geology and Geophysics from Yale University, New Haven, Connecticut in 1972. I received a PhD in Geology and Geophysics from Yale University, New Haven Connecticut in 1975. Since 1995 I have been a Fellow of the Optical Society of America. From August, 1975 to March, 1977 I was employed with Yale University, as a Research associate. From April, 1977 to December, 1988 I was employed with Allied Chemical Corporation (which subsequently changed their name to Allied Corporation, then Allied-signal Corporation and finally Honeywell

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corporation), as a Research chemist and was promoted to Senior research associate. From January, 1989 to present date, I have been employed by the Center for Research and Education in Optics and Lasers(CREOL) at the University of Central Florida, in Orlando, Florida as a tenured member of the faculty. From January, 1989 to present date I have been employed by the University of Central Florida in Orlando, Florida as a Professor of Physics, a Professor of Electrical and Computer Engineering, a Professor of Mechanical Engineering, and as a Professor of Aerospace Engineering. From June, 1995 to the present time, I have also been employed with Crystal Photonics Inc. of Sanford, Florida as the founder, the Chairman of the Board, the President and Chief Executive Officer.

My primary areas of research include (a) rare earth and transition metal-doped solid-state laser materials; (b) nonlinear optical crystals; (c) scintillating crystals for medical imaging; (d) piezoelectric crystals for acoustic resonators and filters; and (e) novel substrate materials and free-standing single crystal GaN substrates the epitaxial thin film growth of GaN for light emitting diodes and laser diodes.

I have been an inventor and co-inventor on some twenty-one issued United States Patents. I have authored and co-authored over 200 publications in the research areas stated above.

3. Under my direction and control, the claimed invention was reduced to practice prior to February 18, 1999. The invention is encompassed by subject invention claim 1 of "A scintillator detector for high energy radiation comprising : a monocrystalline structure of cerium doped lutetium yttrium orthosilicate, $\text{Ce}_{2x}(\text{Lu}_{1-y}\text{Y}_y)_{2(1-x)}\text{SiO}_5$ where $x = \text{approximately } 0.00001$ to approximately 0.05 and $y = \text{approximately } 0.0001$ to approximately 0.9999." The invention is further defined by subject claim 5 of "A scintillation detector assembly comprising: a cerium doped lutetium yttrium orthosilicate mono crystal; and, a photon detector coupled to said crystal, wherein an electrical signal is generated from the photon detector in response to said crystal being exposed to a high energy gamma ray." and the invention is further defined by subject invention claim 10 of "A method of detecting energy with a scintillation detector, comprising the steps of: receiving radiation by a crystal comprising cerium doped lutetium yttrium orthosilicate;

detecting photons with a photon detector coupled to the crystal." In order to more fully understand the invention, a definition of the scintillating process will now be described.

Scintillating is a process to detect high energy radiation by first capturing the radiation and then converting to low energy photons which are then reabsorbed by emitting centers and finally re-emitted as visible lights which are finally detected by the photo-multipliers or photo-detectors. Although the scintillating process is well known it would be very difficult to form a "good" scintillating detector. The ideal detector would require: (a) high density and high atomic weight element to capture the high energy radiation, (b) efficient to down conversion of a single high energy radiation event (*note: We treat high energy radiation as both energy and particles due to the due nature of light in quantum mechanical sense.) to many low energy photons, (c) no color centers or other non-radiative emission centers to take the energy and convert to heat without radiative emission, (d) fast transfer and capture of the low energy photons by the emitting centers, (e) high radiative (quantum) efficiency of the emitting centers, (f) fast decay time of the emitted light, and (g) high transparency of the emitting medium so that light can be guided to the photo-detectors without scattering loss. In this case, monocrystal particles are necessary. It is not possible to use polycrystalline ceramic powder or sintered ceramic blocks unless the material is cubic in symmetry. Unfortunately, none of the material of interest is cubic in symmetry. In addition, the material should be rugged, none-hygrosopic and capable to produce in large quantities (by the tons) at low cost. To be able to find a material that can satisfy all these requirements to make the detector would not be well known nor obvious.

Cerium doped lutetium yttrium orthosilicate, $\text{Ce}_{2x}(\text{Lu}_{1-y}\text{Y}_y)_{2(1-x)}\text{SiO}_5$, (or LYSO) monocrystal has the versatility to satisfy all these requirements and out perform pure cerium doped lutetium orthosilicate in light yield making it unique. Such a detector would not be obvious.

The significant part of the detector invention is the discovery of cerium doped lutetium yttrium orthosilicate, $\text{Ce}_{2x}(\text{Lu}_{1-y}\text{Y}_y)_{2(1-x)}\text{SiO}_5$ (LYSO) monocrystal for use as a high light yield and fast decay scintillator for high energy radiations. The most significant contributions of our

work was (1) to demonstrate the ability to produce large size LYSO monocrystals with any lutetium to yttrium ratio and still retain the uniform crystal composition from top to bottom using essentially all the melt available for growth and (2) to increase the light yield over cerium doped pure lutetium orthosilicate. Both of these features are unique and not obvious from just looking at the simple mixing of lutetium and yttrium within the crystal structure.

I have been studying the radiative emissions of both transitional metal elements and rare earth elements for over 20 years because of my research interest in laser crystals. My involvement in scintillating material research started back in 1994. My first involvement was exactly on the cerium doped lutetium orthosilicates (LSO) when I was hired as a consultant for Dr. Melcher, the inventor of LSO, of Schlumberger corporation. I was asked to look into different aspects of the crystal growth process of LSO as well as the reasons for a frequently large variation in light yield among crystals grown in different batches. In addition to my company now being the largest producer of the LSO crystal, my company has also developed the process to grow cerium doped gadolinium orthosilicate (GSO) single crystals. As such, we are now also the largest commercial producer of GSO crystals. And now my company has established the process for mass producing the LYSO crystals. Our company is specialized in the growth of high melting temperature ($> 2,000^{\circ}\text{C}$) refractory crystals and now has substantial knowledge and experience to produce all types of cerium doped rare earth orthosilicates for scintillators.

Our original idea to develop the LYSO crystal was trying to reduce the cost of manufacture of pure LSO crystal. When we just started the work on LSO crystals, the cost of lutetium oxide (Lu_2O_3) was very expensive, over \$4,000 per kilogram. We worried that the finished LSO crystal will be too expensive to be acceptable by the commercial market. The idea is to substitute lutetium with cheaper elements without sacrificing the performance. Because of the constraints of crystal structure, ionic size and charge within the structure, absence of absorption and emission centers, the tolerance of high melting temperature ($2,200^{\circ}\text{C}$) without evaporation, there would be only three elements that can satisfy these requirements, which would include gadolinium (Gd), scandium (Sc) and yttrium (Y).

The element gadolinium would be too large in ionic size to be useful. In fact, pure gadolinium orthosilicate (Gd_2SiO_5) has a totally different crystal structure. Only limited substitution of gadolinium in LSO is possible without seriously degrading the crystal quality. This limited substitution of gadolinium is substantially different than the Melcher patent but does not achieve our purpose to reduce the material cost. Scandium has a slightly smaller ionic size than lutetium but scandium oxide (Sc_2O_3) is more expensive than lutetium oxide at \$6,000 per kilogram. Substituting lutetium by scandium makes the crystal even more expensive and thus totally defeats the purpose. Yttrium can have a total solid solution with lutetium and yttrium oxide is quite cheap at around \$100 per kilogram. Thus it is the ideal material for substitution. However, yttrium is too light with the atomic number of 39 and atomic weight of 89 as compared with lutetium with atomic number of 71 and atomic weight of 175. Large substitution of lutetium by yttrium will reduce the crystal density and thus stopping power. Fortunately, the stopping power does not drop linearly with yttrium substitution (see our patent disclosure), we can in fact substitute up to 70% of lutetium in the LYSO crystal and still has adequate stopping power. Therefore LYSO has achieved our original purpose to reduce the material cost.

We initially started a first growth of the LYSO single crystal and have subsequently done a lot of more detailed work on the crystal. We were surprised by two observations:

- (1) The distribution coefficient of both yttrium and lutetium are near unity within the crystal.

This is quite a surprise given the large difference in atomic weight and some but significant difference in ionic size and the complex structure of LSO with two different rare earth sites. These two ionic sites have different size and oxygen coordination number. The near unity distribution coefficient makes it possible to produce LYSO crystals with any lutetium to yttrium ratio and to convert essentially all the melt into crystal without worrying about the change in crystal composition from top to bottom and to avoid the possibility of cracking.

- (2) The light yield of cerium doped LYSO monocrystal is actually higher than that of cerium doped LSO.

Simple dilution of LSO with yttrium is good for a cost reduction. In addition, the ability to produce large single crystals with uniform composition and with improved light yield would be unique enough to be both novel and unobvious. We have illustrated both of these facts in our patent disclosure.

4. I am familiar with U.S. Patent 4,958,080 to Melcher which was cited with the filing of the present patent application. This patent describes a "Lutetium Orthosilicate Single Crystal Scintillator Detector", title, of "cerium-activated lutetium oxyorthosilicate...", column 4, lines 9+, which does not include "yttrium." Melcher's detector also includes powders having different ratios than the present invention.

5. I have carefully reviewed Great Britain Patent Specification 1,336,518 to Watanabe et al. which describes a "Phosphor Material", title, which can include "cerium activated yttrium silicate", page 1, lines 16-17. I disagree with the statements in Official Action dated March 8, 2002 that "...it is known from Watanabe et al., that a cerium doped lutetium yttrium orthosilicate phosphor is even more promising in terms of its scintillation properties (Table IV) as the cerium doped lutetium orthosilicate prepared by Melcher....it would have been obvious to one having ordinary skill in the art...to modify the monocrystalline structure..of Melcher to have it comprise the luminescent material suggested by Watanabe et al. in view of the reasonable expectation of success based on the higher luminescence activity....reported therein." I further disagree with the other statements raised in the Official Action as to why additional claimed limitations would also be obvious.

6. In my opinion the "Mole ratio" of "Lutetium oxide", "Yttrium oxide" and "Silicic anhydrite" referred to in Table II of Watanabe which is used for the phosphor composition would not yield a "monocrystalline structure of cerium doped lutetium yttrium orthosilicate" which has been repetitively claimed in the present invention. In my opinion, the "mole ratio" of Table II of Watanabe will not produce a single monocrystalline structure.

I understand that the examiner raised the issue of the British Patent 1,336,518 by Watanabe et al. that they prepared the ceramic powder by sintering the following composition

(according to the Table II of their disclosure), $\text{Ce}_{0.04}(\text{Lu}_x\text{Y}_{1-x})_{2(1-0.02)}\text{Si}_3\text{O}_9$, at 1350°C for 4 hours without melting. The sintered powder shows improvement of luminescence when excited by a 10 KV electron beams as compared with pure lutetium end members. One should notice that the pure lutetium end member of Watanabe's receipt in Table II should have the composition of $\text{Ce}_{0.04}(\text{Lu})_{2(1-0.02)}\text{Si}_3\text{O}_9$, which is very different from Melcher's disclosure in U.S. Patent 4,958,080 of the composition of cerium doped lutetium orthosilicate, $\text{Ce}_{2x}\text{Lu}_{2(1-x)}\text{SiO}_5$. Since there is no phase diagram for the LYSO system, according to the known phase diagram of yttrium orthosilicate which has the same crystal structure as LSO and LYSO crystals, Watanabe's sintered powder will transform into a mixture of two compounds, $\text{Ce}_{0.04}(\text{Lu}_x\text{Y}_{1-x})_{2(1-0.02)}\text{Si}_2\text{O}_7 + \text{SiO}_2$. The luminescence compound described by Watanabe is actually cerium doped lutetium yttrium di-silicate and not orthosilicate (or mono-silicate). It is totally fortuitous that the di-silicate shows the same luminescence behavior as orthosilicate since the two compounds have totally different crystal structures.

7. In the prior art cited there was no expectation to create monocrystalline structures such as that of the present invention. As I have mentioned above Watanabe's composition has too much excess in silica to be useful. Sintered powder will have the lutetium yttrium di-silicate compound mixed with pure silica. High silica content in any mixture will make the melt extremely viscous and glass forming. In fact, the growth of the stoichiometric lutetium yttrium di-silicate compound would be already extremely difficult because of the high silica content. Watanabe's composition is even more silica rich and shifts further into a totally incongruent region. This makes the growth of single crystal totally impossible. Even if one can grow a crystal, it will be the di-silicate crystal and not the ortho-silicate what we have invented. In fact, it is highly likely that the melt of Watanabe's composition is glass forming. I was not familiar of the existence of Watanabe's work when we conduct our research work. However, even if we had knowledge of this patent its' teachings would have to be ignored since by our experience it is not a workable composition for crystal growth even though it is perfectly all right to make sintered ceramics through solid state reactions.

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8. In my opinion and based on my experience the extra moles of Watanabe when combined with Melcher will produce a mixed phase and not a single monocrystalline crystal structure. Since Watanabe's composition is totally different from Melcher's composition with so much excess in silica, it has shifted the composition further away from the congruent stoichiometric composition of the orthosilicate. Based on the phase diagram, Watanabe's composition can only produce di-silicate crystal at best. This is not the orthosilicate that we have invented in our patent application.

Based on my opinion and vast research experience in these areas it would not be obvious to a person of ordinary skill in the art to combine Melcher and Watanabe in order to create a single monocrystalline crystal structure such as that of the present invention.

9. I further declare that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Brian S. Steinberger, PhD

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Brian S. Steinberger
Law Offices Of Brian S. Steinberger, P.A.
Registered Patent Attorney
Reg. No. 36,423
101 Brevard Avenue
Cocoa, Florida 32922
(321) 633-5080